METHOD FOR THE DETERMINATION OF THE MINERAL COMPOSITION OF SEDIMENTARY MANGANESE OXIDE ORES ON THE BASIS OF THEIR THERMAL PROPERTIES

GY. GRASSELLY and EVE KLIVÉNYI

(Institute for Mineralogy and Petrography of the University, Szeged)

ABSTRACT

To elucidate concerning the genetical and geochemical conditions of the sedimentary manganese ore deposits is essential to examine the correlations of the grade of oxidation of the Mn-ores, the redox-potential and the pH of the environment. The first step to reach it is not to know merely the whole MnO and active O contents of the manganese oxide ores but to know their distribution among the mineral components of the ores to be taken into consideration, i. e. the actual quantity of the mineral components contained in the sedimentary manganese oxide ore samples examined.

In the present paper the authors suggest a method for the determination of the mineral composition based on the thermal properties of the manganese oxide minerals using a graphic plotting as well. Employing this method the quantity of pyrolusite, manganite and psilomelane to be found near each other simultaneously in the sedimentary Mn-oxide ores in Hungary has been determined.

INTRODUCTION

For the further completion of the establishments concerning the conditions of the formation of sedimentary manganese ore deposits in Hungary the systematic examinations relating to the correlations between the pH and redox-potential of the environment and grade of oxidation and composition of the manganese oxides and oxide hydrates, respectively, will furnish valuable data.

In his book *Szádeczky*[11] emphasised the geochemical importance of the grade of oxidation and also assumes that theoretically the grade of oxidation could be characterised not merely by the ferro-ferri ratio, but also by that of other elements of variable valency, e. g. MnO_2/MnO (O Mn). At the examination of manganese oxides the application of this assumption seems very evident. However, the determination of the grade of oxidation of heterogeneous ore associations by the giving of the MnO_2/MnO ratio or that of the whole MnO and active O content is not sufficient, but a means must be found to determine the quantitative ratio of the single manganese oxides of the ore assemblages too.

The mineral composition of a heterogeneous sedimentary manganese ore cannot be determined only on the basis of the data of the chemical analyses, but ore microscopic investigations are not either able to show precisely in every case the quantitative ratio of the single components. However, the quantitative determination of the oxidation grade, as well as that of the ratio of the individual components of the ore associations could partly compose the basis for further geochemical considerations and render possible the precise definition of the ore samples, generally considered as pyrolusites and psilomelanes, respectively. Thus, more precisely defined types may be distinguished in the mineral associations of the sedimentary manganese oxide deposits.

The authors have already dealt in several papers[5,6] with the thermal properties of manganese oxides of higher valencies, one of them has also elaborated a procedure for the determination of the composition of the MnO_2—Mn_2O_3—Mn_3O_4 systems[3]. So far the examinations have been carried out exclusively with artificial pure oxides identified by X-rays in order to eliminate as far as possible the interfering impurities and to be able observe in mixtures of definite composition the interaction of the various manganese oxides of higher valencies during the thermal treatment. The DTA examinations[2] of pure oxides and their mixtures respectively were dealt with by *Mrs. M. Földvári Vogl* and *Miss V. Koblencz.*

The results of the thermal examinations rendered necessary and also possible the modification[4] of the originally suggested method[3] for the determination of the composition of the MnO_2—Mn_2O_3—Mn_3O_4 systems. The experiences gained by examinations of artificial oxides rendered it also possible for the authors to attempt the quantitative determination of the mineral composition of the fairly variable highly impurified sedimentary manganese oxide ores. An attempt to find a suitable solution seemed all the more necessary because the thermal curves obtained at the DTA examinations of the samples containing besides the various manganese oxides clayey limonitic impurities in considerable amounts cannot be unequivocally evaluated in most of the cases — mainly not in a semi-quantitative manner.

The modified method suggested for the simultaneous determination of the three manganese oxides of higher valencies can according to the data of the paper cited above[4] be applied advantageously in presence of MnO_2, Mn_2O_3, Mn_3O_4, i. e. that of pyrolusite, manganite and hausmannite. However, in the case of the examination of the mineral composition of the sedimentary manganese ore deposits in Hungary this is somewhat more complicated. Inasmuch, as in addition to the presence of pyrolusite that of psilomelane must also be taken into account. Hausmannite may be neglected considering that the works dealing with the mineral associations of the Hungarian sedimentary manganese ore deposits do not mention their occurrence anywhere.

Thus, the first question which must be decided is whether and how the quantitative method hitherto applied for the artificial pure oxides and their mixtures can also be used in the case of the pyrolusite-manganite-psilomelane association.

EXPERIMENTAL

A. On psilomelane and its thermal behaviour

In the course of their detailed investigations of various artificial and natural manganese oxides *Rode* and his co-workers[10] dealt with the examination of complex compounds containing besides Mn^{IV} also Mn^{II} and foreign metals too. Considering these compounds as derivatives of metamanganous acid — $MnO_2 . H_2O$ — and polymetamanganous acid — $nMnO_2 . H_2O$ — respectively, they termed them permanganites and polypermanganites, respectively.

They give the formula: $(R, Mn)O . nMnO_2 . mH_2O$ for polypermanganite, where R may be K_2, Na_2, Ca, Ba, Pb, respectively. Many samples of different localities considered to be psilomelanes were examined. On the basis of the thermal and X-ray examinations some of the samples proved to be pyrolusite, or a mixture of pyrolusite and braunite. According to the chemical and X-ray examinations, however, the greater part of the samples proved to be a mixture of pyrolusite (more precisely the β and γ modification of MnO_2) and polypermanganites. In 8 of the samples the presence of potassium polypermanganite and in a sample from Saxony that of barium polypermanganite could be established. The former corresponds to cryptomelane, the latter to hollandite.

Mineralogically the hard manganese ores of high percentage with a botryoidal-reniform habit probably precipitated as gel used to be in general termed under the collective name of psilomelane.

Of these, however, very many as has been shown by numerous examinations — are nothing else than mixtures of various manganese oxides. It has, however, also been established, that »psilomelane in the strict sense of the word« really exists too. Recent investigations have also shown that even the psilomelane mentioned above is not uniform, but that psilomelanes contain apart from »original psilomelane« also cryptomelane, however, hollandite and coronadite isomorphus with the latter may also occur. According to the establishments of *Ramdohr*[9] the three latter components can be difficultly distinguished by ore microscopic examinations from the »original psilomelane«.

The composition of the »original psilomelane« is expressed by the following formula: $BaMn^{II}Mn_8^{IV}O_{16}(OH)_4$. The high barium content of the mineral belongs to the lattice. The composition of cryptomelane, hollandite and coronadite is given by the following formula: $XR^{II}Mn_6^{IV}O_{14}$ where X=K, Ba, Pb; R^{II}=Mn, Fe, Cu, Zn. The cryptomelane contains mainly potassium, barium is absent, or only present in insignificant amounts, the coronadite may contain X = Pb and the hollandite Ba. Their properties are fairly similar the three members may form isomorphus mix-crystals. In his earlier work *Ramdohr* termed collectively these three components as the second component of psilomelanes. According to the present establishments of *Ramdohr* psilomelanes contain three main crystalline components. In addition to these almost always pyrolusite may be found too.

Rode[10] states that the thermal curves of polypermanganites are in general characterised by a peak indicating the giving off of water and an exotherm peak due to a recrystallization reaction followed by an

endotherm peak corresponding to the decomposition of polypermanganite. It may be remarked that, in the case of natural recrystallized polypermanganites, i. e. psilomelanes, the exotherm peak mentioned of course fails to occur. According to *Rode* cryptomelane decomposes at 750—850° C, thus at a higher temperature than the β- or γ-modification of MnO_2, not Mn_2O_3 (α-kurnakite), but a new crystalline compound is built up.

On the thermal curve of psilomelane described by *Kulp* and *Perfetti*[8], at about 700°C and 800°C an endotherm broadening may be observed and somewhat over 1000°C a more definite endotherm peak too. In the case of coronadite *Caillère* and *Kraut*[1] observed endotherm peaks at 740°C and 1000°C, respectively.

The psilomelane found in the zone of oxidation of Rudabánya in mine Andrássy II. is according to the chemical analysis very similar to the ideal composition of the »original psilomelane« so much so that in Hungarian relation the psilomelane from Rudabánya may be considered to represent the ideal psilomelane.

	$H_4BaMnMn_8O_{20}$	Psilomelane Rudabánya
MnO_2	72,77%	65,68%
MnO	7,42	9,74
Fe_2O_3	—	1,11
Al_2O_3	—	0,45
BaO	16,04	16,87
CaO	—	1,20
MgO	—	1,07
K_2O	—	traces
Na_2O	—	traces
H_2O+	3,77	3,74
SiO_2	—	0,67
	100,00%	100,53%

According to *S. Koch*[7] the psilomelane from Rudabánya forms a reniform layer on limonite the very fine stratification of the former runs parallel to the surface. It consists of an entangled texture of fine threads which cannot even be detected with high magnification, in some places several bigger single threads running perpendicularly to the layers and their radiated aggregations, respectively, may be observed.

The aim of the present paper is to find a method for the determination of the mineral composition of sedimentary manganese oxide ores, generally composed of pyrolusite-manganite-»psilomelane«. The thermal behaviour of the components of MnO_2 and Mn_2O_3, respectively, corresponding to pyrolusite and manganite is already clear. In one of their papers[6] the authors have established on the other hand, that Mn_3O_4 which is alone in a pure state actually the most stable oxide of manganese at higher temperatures, takes up also in the presence of small amounts of MnO_2 and/or Mn_2O_3 already at lower temperatures oxygen from the air, and at 560—700°C transforms completely into Mn_2O_3. This is supported by the DTA examinations of *Mrs. Földvári* and *Miss V. Koblencz*[2] and also confirmed by the X-ray investigations of *K. Sasvári*.

1	2	3	4	5		6
Samples and locality	Sample No on the diagram Fig. 4.	Thermal curve No	Original MnO + O content of the samples in per cent	MnO and O content of the sample recalculated to 100 per cent		
				At 25°C		Ignited at 7
				MnO	O	MnO
Pyrolusite Mád	1	2—1	42,02	83,22	16,78	89,23
Pyrolusite Eplény	2	2—2	53,30	83,00	17,00	87,25
Pyrolusite Eplény	3	2—3	33,42	83,21	16,79	86,58
Pyrolusite Almagyar	4	2—4	55,76	81,94	18,06	89,50
Pyrolusite Eplény	5	2—5	45,88	82,65	17,35	86,65
Pyrolusite Eplény	6	2—6	58,33	83,15	16,85	86,06
Psilomelane Rudabánya	7	3—7	76,84	83,72	16,28	83,78
Psilomelane Urkút	8	3—8	75,15	82,98	17,02	85,42
Psilomelane Urkút	9	3—9	72,89	83,12	16,88	88,88
Psilomelane Urkút	10	3—10	51,09	82,71	17,29	86,27
Psilomelane Urkút	11	3—11	68,37	87,90	12,10	89,37
Psilomelane Lábatlan	12	3—12	76,98	89,42	10,58	89,40
Crust of a concretionary psilomelane Urkút	A	—	23,34	83,11	16,89	89,49
Core of a concretionary psilomelane Urkút	B	—	37,49	83,30	16,70	85,20
Wad brownish layer Urkút	C	—	39,23	85,01	14,99	89,85
Wad bluish-black layer Urkút	D	—	53,82	85,99	14,01	89,91

e I.

	7	8				9		
	Δ O%	Distribution of the MnO + O content (recalculated to 100%) of the samples among the molecules: (Composition plotted on diagram of Fig. 4.)				Calculated mineral composition of the original samples in weight %		
		MnO_2	Mn_2O_3	$H_4BaMnMn_8O_{20}$	O% calculated	Pyrolusite	Manganite	Psilo-melane
	—6,01	73	15	12	16,95	30,67	7,01	6,28
	—4,25	52	6	42	17,18	27,70	3,55	27,90
	—3,37	41	7	52	16,92	13,70	2,59	21,66
	—7,56	92	—	8	18,26	51,29	—	5,56
	—4,00	47	2	51	17,36	21,56	1,01	29,16
	—2,91	35	3	62	17,09	20,41	1,95	45,09
	—0,06	1	4	95	16,44	0,76	3,42	91,01
	—2,44	29	—	71	17,18	21,79	—	66,52
	—5,76	69	11	20	17,15	50,29	8,92	18,16
	—3,65	42	1	57	17,29	21,45	0,56	36,31
	—1,47	17	75	8	12,05	11,62	57,10	6,80
	+0,02	—	94	6	10,53	—	80,56	5,74
	—6,38	77	12	11	17,21	17,97	3,12	3,19
	—1,90	23	6	71	16,68	8,62	2,49	33,18
	—4,84	59	40	1	15,07	23,14	17,47	0,48
	—3,92	47	53	—	14,02	25,92	31,76	—

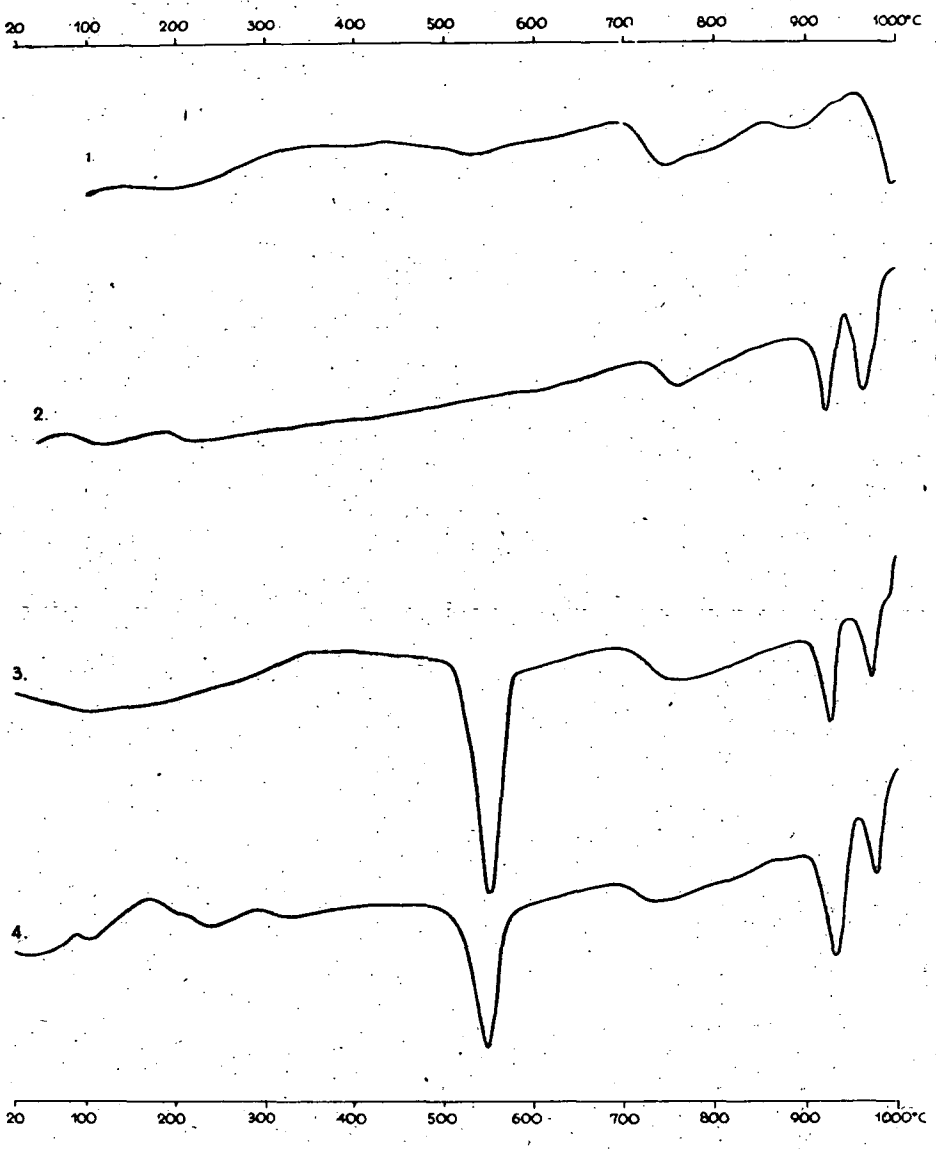

Fig. 1. Thermal curves of psilomelane from Rudabánya and that of its mixtures with artificial Mn_2O_3 and/or MnO_2

1—1	Psilomelane, Rudabánya	
1—2	Psilomelane + artificial Mn_2O_3	1:1
1—3	Psilomelane + artificial MnO_2	1:1
1—4	Psilomelane + artificial MnO_2 + Mn_2O_3	1:1:1

On the thermal curve of the psilomelane from Rudabánya (1—1) around 750°C the first definite endotherm broadening can be observed, and at about 890°C another weaker one. At 1000°C the beginning of the formation of a sharp endotherm peak may be seen. Below 700°C an essential change on the thermal curve, mainly indicating the decomposition of psilomelane, cannot be found.

The ratio of the MnO and active O content of the psilomelane does not either change if the sample is ignited at 650—700°C during three hours. This fact, as well as the thermal curve demonstrate that below 700°C there has not occurred any change in the grade of oxidation of psilomelane, i. e. in the ratio of the MnO and O content.

It was, however, questionable whether or not psilomelane behaves in the presence of MnO_2 and/or Mn_2O_3 like Mn_3O_4, i. e. undergoes in the presence of the above oxides at temperatures below 700°C any change, either by giving off or taking up oxygen.

To decide this question psilomelane from Rudabánya was mixed with artificial Mn_2O_3 and artificial MnO_2 respectively, in a ratio 1:1 and finally with both oxides in a ratio 1:1:1. The corresponding thermal curves are 1—2, 1—3, and 1—4. The thermal curves of the mixtures show that at temperatures below 700°C psilomelane does not either change in the presence of considerable amounts of Mn_2O_3 and/or MnO_2. On the curves of the mixtures the first pronounced endotherm broadening characterising psilomelane appears at about 750°C at the same place.

However, according to the thermal curves it seems that at higher temperatures in the presence of Mn_2O_3 (either if it was originally also present in this form or if it formed from MnO_2 at 560°C which is demonstrated on the curves 1—3 and 1—4 by a sharp endotherm peak) psilomelane already undergoes a far more significant decomposition. Most probably the endotherm peak appearing sharply on the curves of the mixtures at 920°C may be interpreted by this fact. It may be assumed that the second sharp endotherm peak appearing at about 980°C is the result of the transformation of the manganese oxides into Mn_3O_4. The decomposition occurring at 920°C of psilomelane in mixtures may be due to the fact that its complete decomposition into Mn_3O_4 — which in a pure state only starts at 1000°C — already takes place in mixtures at about 980°C.

The pure psilomelane, as well as the mixture of psilomelane and MnO_2 in a ratio of 1:1 ignited at 950°C gave a reddish-brown ignition product resembling Mn_3O_4 obtained by ignition of various manganese oxides at high temperatures. On determining the MnO and O contents of the products obtained by ignition and recalculating them to 100 per cent, if the starting substance was pure psilomelane $MnO_{1,4}$, i. e. $Mn_3O_{4,35}$ and if the starting substance was a mixture of MnO_2 and psilomelane the composition obtained was $MnO_{1,37}$ i. e. $Mn_3O_{4,11}$. The composition of the ignition product obtained at 950°C is in good approximation with the composition of Mn_3O_4. It could also be established that the composition of the mixture approximates more this ideal composition than the ignition product of pure psilomelane. This fact is also in good agreement with what has been said above relating to the thermal curves of pure psilomelane and its mixtures, respectively.

The essential fact which is of interest at present in these investigations is that the oxidation grade of psilomelane in the presence of MnO_2 and/or Mn_2O_3 at temperatures below 700°C does not change, however, the decomposition of the MnO_2 component of the mixture already takes place at 560°C.

B. The thermal examination of some sedimentary manganese oxide ores.

a) The establishment of the mineral composition of pyrolusite-manganite-»psilomelane« systems.

One of the authors reported[3] in 1955 a procedure for the determination of the mineral composition of the MnO_2-Mn_2O_3-Mn_3O_4 systems. This procedure was based on establishments described in the literature that Mn_3O_4 is the more stable oxide of manganese at higher temperatures and that Mn_2O_3 transforms only at 950°C into Mn_3O_4, whereas MnO_2 already transforms at 560°C into Mn_2O_3 by giving off oxygen. Hence, according to this assumption at 700° C only MnO_2 changes, the other two oxides remain unchanged. Consequently, the difference between the active oxygen content of the original sample and that of the ignited one would be proportional to the MnO_2 content of the substance. Thus it seemed possible to establish by means of suitable graphical plotting the composition of any ternary system. However, on te basis of the further examinations of the authors just this suggested method had to be modified, as it could be proved that in the presence of the two other oxides, Mn_3O_4 did not remain unchanged, and since then a new method[4] without graphic plotting had been elaborated for the determination of the composition of the above systems.

Concerning the pyrolusite-manganite-psilomelane systems, however, according to what has been demonstrated above, of the three components psilomelane remains even in the presence of the two other oxides unchanged at 700°C, manganite only gives off its water content at about 350°C and otherwise remains unchanged as Mn_2O_3 till 950°C, only pyrolusite decomposes already at about 560°C. Thus among the three components when they are ignited in free air at temperatures below 700°C, only one is variable: the pyrolusite. This means that the trend of thought of the method earlier proposed by one of the authors for the determination of the composition of the MnO_2-Mn_2O_3-Mn_3O_4 systems — mutatis mutandis — is suitable for the determination of the mineral composition of systems containing the above components with the application of the graphic plotting reported in the paper cited[3] too.

Merely the following modifications of the trend of thought and graphic plotting, respectively, must be carried out: instead of Mn_3O_4 psilomelane is contained in the system, therefore, the place of the oxygen base line must be altered on the graphicon. On the earlier graphicon, instead of the ideal active oxygen content of 6,99 per cent plotted on the ordinate at 100 per cent Mn_3O_4, the ideal oxygen content of 16,70, per cent of psilomelane (the »original psilomelane«) had to be plotted. This value is obtain-

ed if the MnO and O content calculated on the basis of the formula $H_4BaMnMn_8O_{20}$ is recalculated to 100 per cent.

The outlined course of the determination of the mineral composition of the pyrolusite-manganite-psilomelane systems is as follows:

1. The whole MnO and the active O content of the samples is determined.

2. The samples are ignited at 650—700°C and the amount of the active O and MnO is again determined. The latter can already be calculated from the determined MnO content of the original samples too, if the loss on ignition is known.

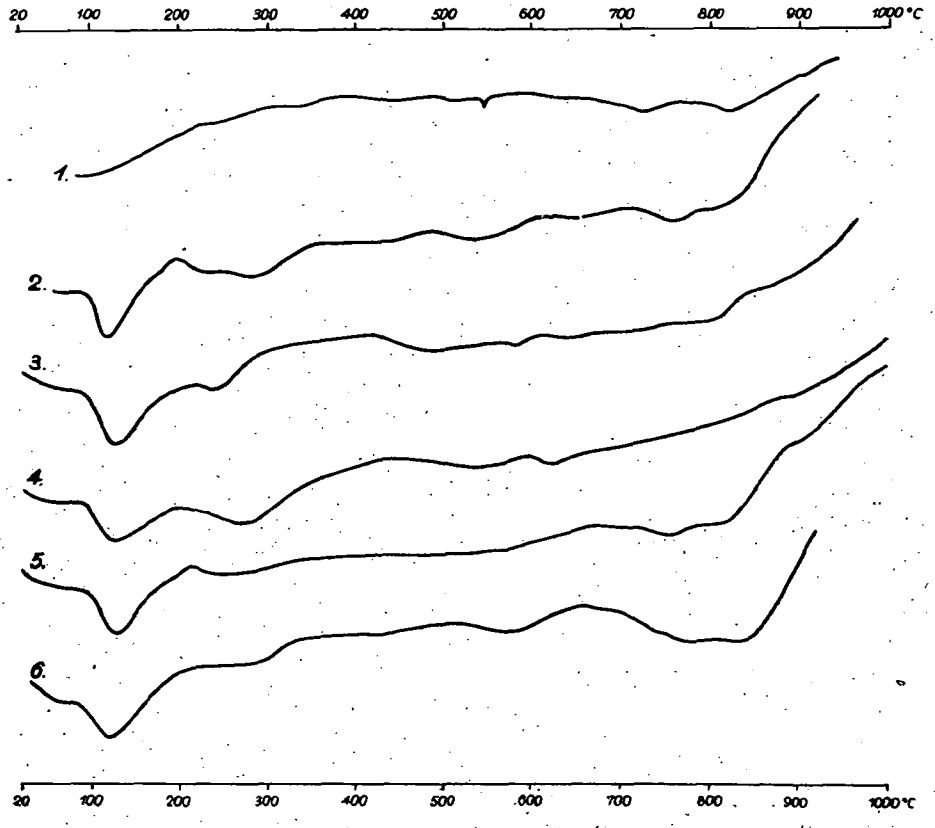

Fig. 2. Thermal curves of some sedimentary manganese oxide ores (Concerning denotations see Table I.)

3. The MnO and O contents of both the original and ignited samples are recalculated to 100 per cent.

4. After the recalculation to 100 per cent the difference between the oxygen contents of the ignited and unignited samples gives the ΔO per cent, the amount of which is proportional to the pyrolusite (MnO_2) content of the mixture.

5. The obtained values are plotted on the diagram and finally on the concentration triangle — belonging to the diagram — each sample is characterised by a dot. This dot characterises the ratio of the manganese oxide components of the given sample, hence on the basis of the site of the dots the various types may be well defined. The dots plotted an the concentration triangle, however, do not give actually the real percentile amount of the manganese oxide minerals of the original samples containing clayey limonitic impurities too.

Considering that the paper mentioned above[3] describes the manner of plotting in detail this question is no more dealt with.

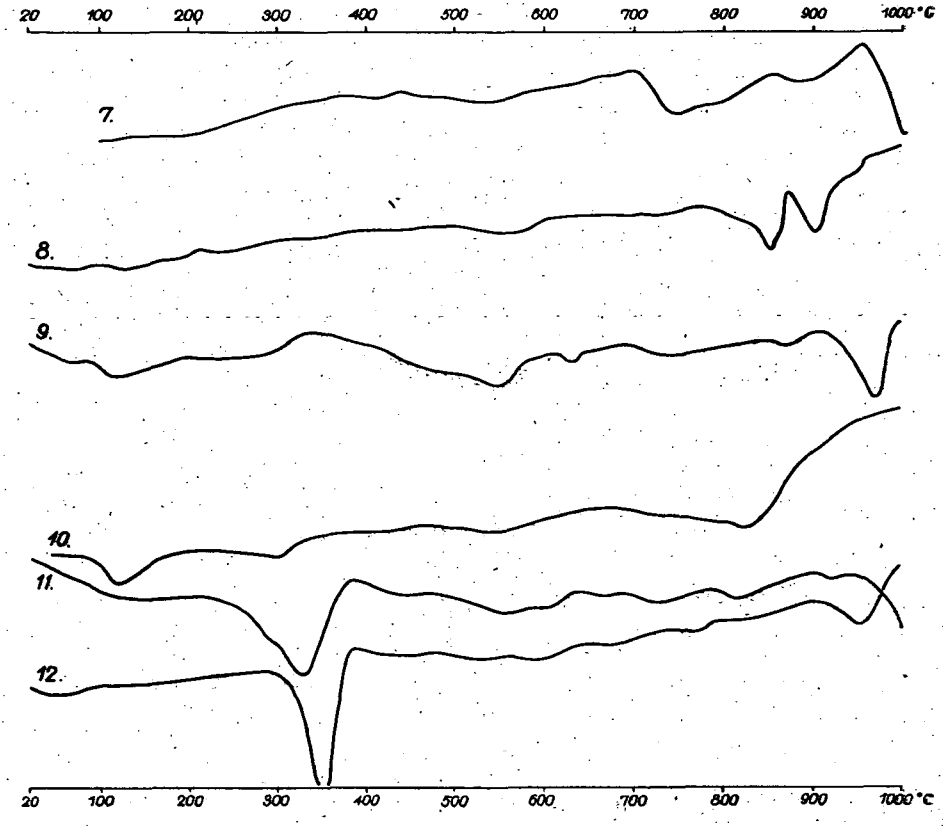

Fig. 3. Thermal curves of some sedimentary manganese oxide ores (Concerning denotations see Table I.)

According to the method described above a few Hungarian ore samples, mainly those from Eplény and Urkut, as well as from Lábatlan, Rudabánya and Almagyar were examined. In our collection the samples were denoted, as customary, under the generalising name of pyrolusite, psilomelane, wad. The result of the examinations are summarised in Table I.

Column 8. of the Table I. contains the data plotted on the diagram of Fig. 4. These data characterise the type of the single samples. Finally, Column 9. of the Table I. shows the most probable mineral composition of the original samples, where »psilomelane« may denote »original psilomelane« as well as cryptomelane, or hollandite and their mixtures, respectively, as these are generally the main components of psilomelanes.

The DTA examination of the samples (1—12) enumerated in Table I. was also carried out. The thermal curves are plotted on Figs. 2. and 3.

The calculated composition given in Column 9. of Table I. was plotted on the concentration triangle of Fig. 4. The different manganite-pyrolusite and psilomelane types can be well distinguished.

b) Discussion of the thermal investigation and the manner of plotting.

It has been mentioned that though the dots plotted on the concentration triangle characterise the various samples, they do not yet represent the real percentile mineral composition.

The determination of the mineral composition of a sample from Eplény denoted as pyrolusite in Table I. under No. 5 represents an exemple for the establishment of the real mineral composition:

The MnO + O content of the sample:	MnO + O	45,88 per cent
The measured MnO and O content recalculated to 100 per cent:	MnO O	82,65 17,35
The MnO and O content recalculated to 100 per cent after heating at 700°C:	MnO O	86,65 13,35
ΔO per cent:		—4,00

On plotting the values obtained (17,35 per cent and 4 per cent), the site of the dot obtained on the concentration triangle represents the distribution of the whole MnO + O content recalculated to 100 per cent among the three components of the sample, i. e. it holds:

MnO_2	47 per cent
Mn_2O_3	2
$H_4BaMnMn_8O_{20}$	51

But the MnO + O of the original sample amounts only to 45,88 per cent, the remainder consists of quartzous clayey limonitic impurities. Hence, the data recalculated previously to 100 per cent must be reduced to this value. The results obtained show the true distribution of the actual

MnO + O contents of the samples among the three molecules mentioned above:

MnO_2	21,56 per cent
Mn_2O_3	0,91
$H_2BaMnMn_8O_{20}$	23,39

Hence, subsequently the most probable mineral composition may be calculated on taking the following into account:

a) The value obtained for MnO_2 corresponds to the amount of pyrolusite too.

b) The value obtained for Mn_2O_3, however, does not give directly the percentile amount of manganite, as the composition of manganite is $Mn_2O_3.H_2O$. On taking the ratio of Mn_2O_3 and H_2O into account, the values obtained for Mn_2O_3 must be multiplied by 0.1138 and the product obtained is added to the value of Mn_2O_3, and in this manner the percentile manganite content of the sample is obtained.

c) Also in the case of $H_2BaMnMn_8O_{20}$ originally only its MnO and O content was considered. On taking its other components into account too the obtained values must be multiplied by 0.247 and the original value increased by this product. Then we have how much psilomelane is contained in the original substance.

In the case of the above exemple, if the corresponding calculations are carried out, we have finally that the »pyrolusite« from Eplény containing 37,92 per cent of MnO and 7,96 per cent of active oxygen, actually contains:

Pyrolusite	21,56 per cent
Manganite	1,01
»Psilomelane«	29,16

If the active oxygen percentage of the ore is calculated on taking the amount of the minerals enumerated and their ideal active oxygen percentage into account, we have 7,95 per cent which is in complete agreement with the actually measured value.

This manner of calculation is in the case of pyrolusite and manganite undoubtedly correct. Namely, from the point of view of the grade of oxidation if either pyrolusite (MnO_2) or perhaps ramsdellite ($MnO_2.H_2O$) and manganite ($Mn_2O_3.H_2O$) or possibly bixbyite ($(MnFe)_2O_3$), respectively, are involved the grade of oxidation, i. e. the ratio of the whole MnO and the active O content remains in both cases unchanged. At the most, at the recalculation to the mineral composition the above differences must taken into consideration. Therefore, on one of the peaks on the concentration triangle the molecule MnO_2 and on the other the molecule Mn_2O_3 were plotted. On the other hand, with respect to the plotting of the $H_2BaMnMn_8O_{20}$ molecule on the third peak this is not quite justified, however, we wanted to express that the MnO-O values characterising the »original psilomelane« were considered.

The question may also arise, whether it is alltogether correct only to take the »original psilomelane« — having the above formula — into account, as for instance cryptomelane is always present, what more, holland-

ite isomorphous with the latter may also be present. If in the case of the three minerals on the basis of their formulae only the MnO and O content recalculated to 100 per cent is taken into consideration we obtain that the active oxygen content of cryptomelane and hollandite is 16,20 per cent, whereas that of the »original psilomelane« amounts to 16,70 per cent, i. e. there is no essential difference in the grade of oxidation. Thus, if only the MnO and O content recalculated to 100 per cent of the samples is plotted on the diagram, the site of the dot obtained on the concentration triangle will characterise precisely the type of the ore samples, the ratio of the components. The fact that the composition and its MnO-O ratio of the »original psilomelane« served as the sole basis for the calculations and that the presence of hollandite and cryptomelane was not taken into account did not cause any appreciable deviation on the diagram, thus it does not change the type essentially.

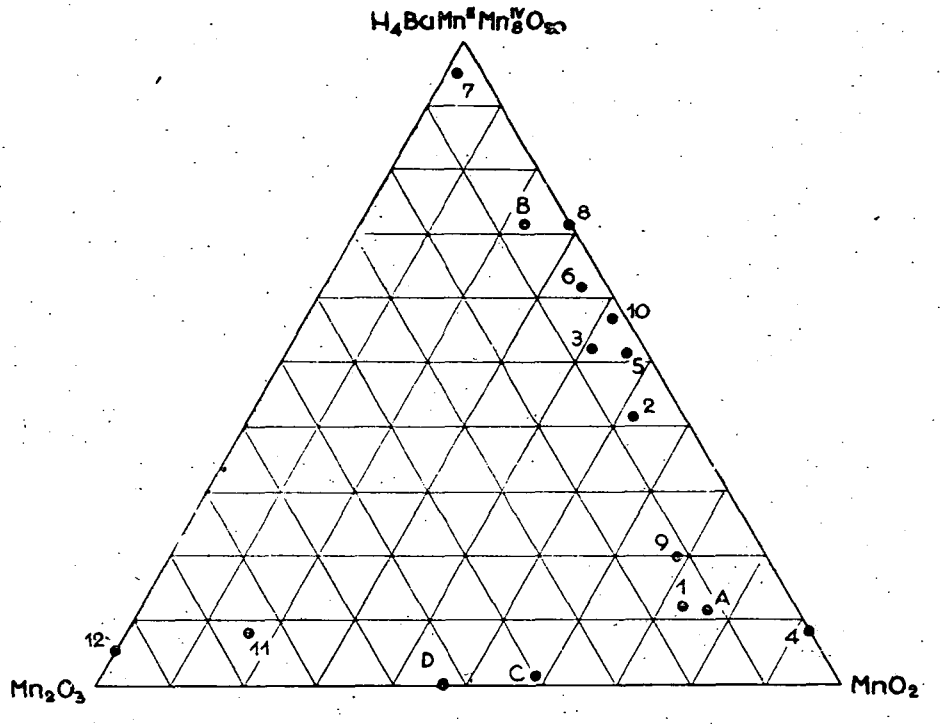

Fig. 4. The distribution of the whole MnO and O content (recalculated to 100 per cent) among the molecules $MnO_2 - Mn_2O_3 - H_4BaMnMn_8O_{20}$ in the samples examined. (Concerning denotations see Table I.)

If the percentile values on the concentration triangle corresponding to the samples are recalculated for minerals the data obtained — taking only MnO-O into consideration — must be multiplied with 0,2740 in the case of »original psilomelane«, whereas if hollandite is involved, the index number would be 0,271 and in the presence of cryptomelane it would be

0,159. On carrying out the above calculations for the sample No. 5 the value reduced to the actual MnO + O content of the original sample must be multiplied by the above index numbers and the original value is increased by this product, then the sample contains

29,72 per cent hollandite or
29,16 per cent »original psilomelane« or
27,10 per cent cryptomelane.

Hence, there is no appreciable deviation, moreover just the calculated amount of the »original psilomelane« seems to be in good approximation with the average of the three various values. At the establishment of the mineral composition the possible errors inherent in the measurings, and subsequent plottings may also cause deviations of about the same extent. In our opinion, thus, if it is also not quite correct to based the calculations only on the »original psilomelane« this affords from the practical point of view a logic and proper aspect concerning the amount of »psilomelane« actually contained in the sample examined.

The thermal curves will not be dealt with in detail, only a few remarks will be added. One establishment is that on most of the curves — with the exception of curves 3—9, 3—11 and 3—12 — the endotherm peak indicating the transformation of manganese oxide components into Mn_3O_4 is absent. Presumably, samples containing clayey impurities abundantly are involved and the exotherm reaction of the various clay minerals taking place at about 980—1000°C is responsible for the absence of the peak mentioned above. According to the examinations two samples proved to be manganite, on the thermal curves of both of them (3—11 and 3—12) the endotherm peak indicating the giving off of water by the manganite appears distinctly at 320 to 340°C. In the samples containing iron impurities this endotherm peak can also be caused by the presence of limonite. It is striking that the peak characterising pyrolusite is hardly visible, it flattens out even in the case of the sample containing pyrolusite in relatively larger amounts. The peaks characterising psilomelane can be detected on several curves, however, it seems in general that the identification merely on the basis of differential thermal curves of manganese oxide components of sedimentary manganese ores containing beside the various manganese oxides clayey-limonitic impurities in considerable amounts too is fairly problematic as the peaks indicating the reactions running down parallel in the course of the heating can overlap, shift or even compensate one another. On the other hand, if the most probable mineral composition is determined in the manner suggested in the present paper, at least the qualitative evaluation of the thermal curves may become easier.

On the basis of the examinations the type of each sample may be precisely determined as well if a sample containing manganese oxides in low percentage as if one containing these oxides in high percentage, or if ore samples of crystalline or earthy habit are involved. Thus, e. g. of a sample considered to be a wad from Urkut the thinner brownish and thicker bluish-black layers of which were separately examined it could be established, that it is a mixture of pyrolusite and manganite (dots *C* and *D*

on Fig. 4.). The crust and interior of a reniform concretionary psilomelane sample from Urkút was also investigated. Pyrolusite (17,97 per cent) dominates in the crust, apart from it there is also a little manganite (3,12 per cent) and psilomelane (3,19 per cent) present, whereas in the interior psilomelane dominates (33,18 per cent) and in addition there also occurs a little pyrolusite (8,62 per cent) and still less manganite (2,49 per cent) (dots *A* and *B* on Fig. 4.). On the other hand, concerning the sample from Lábatlan it could be undoubtedly established that it is dominantly built up of manganite (80,56 per cent) containing a little psilomelane too (5,74 per cent).

This plotting will become particularly useful if it will be possible to plot the composition of an essentially larger number of samples collected from various places and levels of the deposits of Urkut and Eplény as described in the present paper.

In the course of further investigations the authors will deal with the correlation of the composition and grade of oxidation of sedimentary manganese ores and pH value and redox-potential of the medium, respectively, and apply the results for the interpretation of the origin of the Hungarian sedimentary manganese ore deposits.

REFERENCES

1 Caillère, S. and Kraut, F.: Comportement thermique de quelques minéraux manganésifères. — Compt. Rend. Acad. Sci. Paris, 1954, vol. 239, pp. 286—287.

2. Földvári—Vogl, M. and Koblencz, V.: Differential Thermal Analysis of Artificial Manganese Compounds. — Acta Min. Petr. Univ. Szegediensis. Tom. IX. 1956, pp. 7—14.

3. Grasselly, Gy.: The Determination of the Composition of the MnO_2-Mn_2O_3-Mn_3O_4 Systems. — Acta Min. Petr. Univ. Szegediensis, 1955, Tom. VIII, pp. 13—26.

4. Grasselly, Gy.: Remarks on the Determination of the Composition of MnO_2-Mn_2O_3-Mn_3O_4 Systems. — Acta Min. Petr. Univ. Szegediensis, 1956, Tom. IX, pp. 41—46.

5. Grasselly, Gy. and Klivényi, E.: Concerning the Thermal Properties of the Manganese Oxides of Higher Valencies. — Acta Min. Petr. Univ. Szegediensis, 1956, Tom. IX. pp. 15—32.

6. Grasselly, Gy. and Klivényi, E.: On the Stability of the Mn_3O_4. — Acta Min. Petr. Univ. Szegediensis, 1956, Tom. IX. pp. 33—40.

7. Kcch, S. and Grasselly, Gy.: The Manganese Ore Mineral Occurrences of Hungary. — Acta Min. Petr. Univ. Szegediensis, Tom. V. 1951, pp. 1—14.

8. Kulp, J. L. and Perfetti, J. N.: Thermal Study of Some Manganese Oxide Minerals. — Min. Mag. 1950, No. 210, pp. 239—252.

9. Ramdohr, P.: Die Erzmineralien und ihre Verwachsungen. Berlin. 1950, Akademie Verlag.

10. Роде, Е. Я.: Кислородные соединения марганца. (Искуственные соединения минералы и руды.) АК. Н. СССР. Москва, 1952.

11. Szádeczky—Kardoss, E.: Geokémia. Budapest, 1955, Akadémia Kiadó.